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Influence of supplementary irrigation on the amino acid and volatile composition of Godello wines from the Ribeiro Designation of Origin

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ABSTRACT

Concentrations of amino acids and volatile compounds of a given grapevine cultivar might be altered by inter-annual climate variability and management practices such as irrigation. These compounds determine, in part, aroma and sensory characteristics of wines. The current study aimed at assessing the amino acid profile of musts and wines and the volatile composition of wines from *Vitis vinifera* (L.) cultivar 'Godello' grown in the Ribeiro Designation of Origin (NW Spain) under rain-fed and supplementary irrigation (SI) conditions over three years (2012-2014). Supplementary irrigation increased must titratable acidity. However, must amino acid concentrations were not significantly altered by SI. In contrast, the concentrations of ethyl lactate and geraniol were greater in wines from the SI treatment. Significant correlations between amino acids in musts and volatiles in wines were observed. Our results highlight the low impact of SI on must and wine composition, likely due to the low level of water stress experienced by Godello vines. Understanding the effects of SI on wine properties could aid to adapt management practices in the future.

1. Introduction

Amino acids present in grapes and musts play a relevant role in yeast growth and development during alcoholic fermentation. Their concentrations depend on many factors such as grapevine (*Vitis vinifera* L.) cultivar, soil properties, climate conditions and vineyard management (Garde-Cerdán et al., 2014). Some amino acids are precursors of several volatile compounds that contribute to wine aroma: higher alcohols, aldehydes, ketones and esters (Moreno-Arribas & Polo, 2009), which is proven by significant relationships between amino acids and these compounds (Hernández-Orte, Cacho, & Ferreira, 2002).

Climate change is altering the temporal distribution of rainfall and increasing drought events, which raises a great concern in viticultural regions (Fraga, Malheiro, Moutinho-Pereira, & Santos, 2013). As a consequence, irrigation is increasingly being used to cope with the possible negative effects of climate change on berry composition and to minimize interannual variability in yields, even in cool-humid regions such as Galicia, northwest Spain (Cancela et al., 2016). In fact, the concentrations of volatile compounds in grapes vary during ripening depending on temperature and water availability (Robinson et al., 2014). Therefore, irrigation management is a fundamental tool to control berry growth and composition (Jackson & Lombard, 1993).

Irrigation is usual in the viticulture of New World countries, while supplying water to grapevines for wine production was forbidden by law in Spain until 1996 (Ruiz-Sánchez, Domingo, & Castel, 2010). Since then, research has been devoted to determine the effects of several irrigation protocols on grapevine yield and berry composition on red cultivars under water scarcity conditions (Girona et al., 2006; Intrigliolo, Pérez, Risco, Yeves, & Castel, 2012; Romero et al., 2016). In this scenario, the most convenient strategy was to apply moderate water deficits before veraison and irrigating without considerable restriction afterwards (Ruiz-Sánchez, Domingo, & Castel, 2010).

For these reasons, new research is focused on adapting vineyard management (mainly fertilization and irrigation) to improve the concentrations of amino acids in grapes at harvest (Bouzas-Cid, Falqué, Orriols, & Mirás-Avalos, 2018; Canoura, Kelly, & Ojeda, 2018; Teles Oliveira, de Freitas, & Alves Sousa, 2012). However, contrasting results have been obtained, depending on the cultivar and the colour of the

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grapes and on the water stress intensity (Canoura, Kelly, & Ojeda, 2018; Deluc et al., 2009), which is usually low in cool-humid areas (Balint & Reynolds, 2017).

In the Northwest of the Iberian Peninsula (Galicia and North of Portugal), white grapevine cultivars are predominantly grown, and their organoleptic characteristics might be altered by increasing temperatures and drought over the growing cycle. Godello is one of the most important cultivars that are traditionally grown in this region and is used to obtain monovarietal wines that are increasingly being recognised worldwide (Blanco, Mirás-Avalos, Pereira, & Orriols, 2013). The volatile composition of Godello wines has been previously described (Losada, Andrés, Cacho, Revilla, & López, 2011; Versini, Orriols, & Dalla Serra, 1994); however, the amino acid profile of this cultivar, as well as the effect that irrigation might exert on its musts and wines have not been determined. A previous work from our group (Bouzas-Cid, Falqué, Orriols, & Mirás-Avalos, 2018) reported that supplementary irrigation under the climate conditions of Galicia altered the concentrations of several amino acids and volatiles of another white grapevine cultivar, Treixadura. However, the field performance of Treixadura and Godello cultivars was different (Trigo-Córdoba, Bouzas-Cid, Orriols-Fernández, & Mirás-Avalos, 2015); therefore, the concentrations of secondary metabolites (amino acids and volatile compounds) might have also been differently affected by supplementary irrigation, as previously reported for French cultivars (Deluc et al., 2009). Therefore, the aim of the current study was to assess the effects of supplementary irrigation on the amino acid composition of musts and wines, and the aromatic profile of wines from the white grapevine (*Vitis vinifera* L.) cultivar Godello during three consecutive years (2012, 2013 and 2014) in Ribeiro Designation of Origin (DO), Northwest Spain. Studies on the effects of irrigation on amino acid concentrations and their relations with wine aroma are very scarce in the literature, and the current work consitutes an attempt to fill this gap.

2. Materials and methods

2.1. Description of the study site

The present study was conducted from 2012 to 2014 in a 0.2 ha Godello vineyard located in Leiro (42° 21.6′ N, 8° 7.02′ W, elevation 115 m), Ourense, Northwest Spain, within the Ribeiro DO. The vineyard was planted in 1998 with vines grafted onto 196-17C rootstock (deep rooting, well adapted to drought and to acid soils, sensitive to carbonates) on a single cordon system. Rows were East-West oriented; vines were spaced 1.25 m between plants and 2.4 m between rows. Soil was sandy textured, slightly acidic and of medium fertility. The study site can be classified as warm-temperate, sub-humid with cold nights (Supplementary Table 1). Increasing temperatures and decreasing rainfall amounts over the growing season were observed from 2012 to 2014 (Table 1).

2.2. Experimental design in the vineyard

Two treatments were applied in a randomized block design with three replications consisting of three rows with 12 vines each (36 vines per experimental unit).

Treatments consisted of a rain-fed control and a supplementary irrigation (SI) to the 40% of the potential evapotranspiration (ET_o). Water was applied through a drip system from fruit set (end June) to approximately two weeks before harvest (mid-August) (Trigo-Córdoba et al., 2015). Irrigation needs were calculated weekly using data recorded by a weather station located 200 m away from the experimental vineyard and corrected by substracting the rainfall amount registered on the previous week. The inter-year variability of ET_o and rainfall caused that the irrigation amount applied differed from year to year. Therefore, total water amounts applied were 50, 79 and 50 mm for 2012, 2013 and 2014, respectively, allowing for a clear differentiation of grapevine water status under both treatments (Trigo-Córdoba et al., 2015).

2.3. Sampling and winemaking

Grapes from the different treatments were manually harvested on the same day. Vinifications were performed separately on samples of approximately 40 kg per replicate (3 vinifications per treatment and year).

Grapes from each treatment were separately destemmed, crushed and pressed in a pneumatic press (yielding, approximately, 50% must). A replicated 250 mL sample from each treatment was collected for analysis. Pectolytic enzyme was added (4 g hL^{-1}) to favour settling and SO_2 (50 mg L^{-1}) was added to avoid oxidation. After 24 h, musts were racked and fermented in 35 L stainless steel tanks. Commercial yeast (Excellence FW, Lamothe-Abiet, Bordeaux, France) was added (20 g hL^{-1}). Density and temperature of fermentations were measured daily. Once alcoholic fermentation finished, wines were racked and sulphited to 35 mg L^{-1} free sulphur dioxide. A natural clarification was carried out at 4 °C for one month. Finally, wines were filtered, bottled and stored.

2.4. Chemical reagents

Ultra-pure water was generated using Milli-Q equipment (Millipore, Bedford, MA, USA). Super-gradient HPLC grade acetonitrile and methanol were purchased from Scharlau (Sentmenat, Spain). Ammonium chloride was acquired from Merck (Darmstadt, Germany). Amino acid solutions were prepared with HCl 0.1 N using standards purchased from Acros Organics (New Jersey, USA).

Dichloromethane, *n*-pentane and anhydrous sodium sulphate (Scharlau, Sentmenat, Spain) were used for the extraction of free terpenes, volatile fatty acids, ethyl esters, acetates of higher alcohols and C6 alcohols. Standards for volatile compounds were purchased from: Merck (Madrid, Spain), Aldrich (Madrid, Spain), Fluka (Seelze, Germany), Alfa Aesar (Barcelona, Spain) and Sigma (Madrid, Spain). The internal standards (Merck, Madrid, Spain) used were 4-methyl-2-pentanol for the determination of major volatile compounds (methanol, 1-propanol, 2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol, acetaldehyde, ethyl acetate, ethyl lactate, 1-hexanol, acetoine, acetol, 2-phenyl-ethanol, 2,3-butanediol *levo*, 2,3-butanediol *meso*); 4-decanol for terpenes and C6 alcohols; 1-heptanol for volatile fatty acids, ethyl esters and acetates of higher alcohols. All the standards were prepared in 50% hydroalcoholic solutions.

2.5. Analytical methods

Basic parameters of musts (including total soluble solids, pH and titratable acidity) and wines (such as alcohol content and pH among others) were determined by Fourier Transform Infrared Spectrometry (FTIR) using a WineScan FT120 analyzer (FOSS Electric, Barcelona, Spain) calibrated according to the official methods (OIV, 2009). Analytical determinations in wines were carried out in triplicate five months after bottling.

2.5.1. Determination of amino acids in musts and wines

The determination of the amino acids present in musts and wines was carried out through high-performance liquid-chromatography (HPLC) using a method based on a reaction of derivatization in a basic methanolic medium (Gómez-Alonso, Hermosín-Gutiérrez, & García-Romero, 2007). The HPLC analysis was performed using an Agilent 1100 series equipment (Agilent Technologies, Palo Alto, CA, USA). Chromatographic separation of amino acids was carried out in a Zorbax Eclipse AAAcolumn (C18), with a particle size of 5 µm (150 mm × 4.6 mm, Agilent Technologies, Palo Alto, CA, USA). A precolumn was also used (Zorbax Eclipse AAA, 12.5 mm × 4.6 mm;

Table 1
Rainfall amounts and potential evapotranspiration (ET_0) over the growing season (April to harvest) and the irrigation period, including mean temperature, of each year (2012-2014) in the studied vineyard. General attributes of the musts and wines (mean ± standard error) of Godello variety for the three vintages studied (2012, 2013, and 2014) in Ribeiro DO. The significances of the factors year and treatment, as well as their interaction are also shown. R = rain-fed; SI = supplementary irrigation.

Year	Growing season rainfall (mm)	Annual rainfall (mm)	Rainfall during the irrigation period (mm)	Mean temperature over the irrigation period (°C)	Growing season ET_0 (mm)	Irrigation period ET_0 (mm)
2012	313.0	841.2	53.4	20.8	697.8	327.5
2013	163.0	1282.6	21.8	21.8	745.2	347.9
2014	185.4	1301.0	84.2	20.0	739.2	330.0
Year	Treatment	Total soluble solids (° Brix)	Titratable acidity ($g\,L^{-1}$)	pH	Malic acid ($g\,L^{-1}$)	Tartaric acid ($g\,L^{-1}$)
MUSTS						
2012	R	22.5 ± 0.3	7.7 ± 0.4	3.22 ± 0.06	2.5 ± 0.1	8.7 ± 0.5
	SI	22.2 ± 0.3	8.2 ± 0.4	3.14 ± 0.05	2.6 ± 0.1	9.0 ± 0.3
2013	R	24.0 ± 0.5	6.3 ± 0.3	3.28 ± 0.06	2.3 ± 0.2	8.0 ± 0.5
	SI	23.2 ± 1.4	7.2 ± 0.5	3.24 ± 0.07	2.7 ± 0.2	8.2 ± 0.3
2014	R	**24.1 ± 0.2 b**	**6.3 ± 0.1 a**	**3.31 ± 0.01 b**	2.5 ± 0.2	**7.7 ± 0.2 a**
	SI	**23.3 ± 0.2 a**	**6.9 ± 0.1 b**	**3.23 ± 0.02 a**	2.7 ± 0.1	**8.3 ± 0.1 b**
Factorial analysis						
Year		**0.039**	**0.003**	0.075	0.837	**0.029**
Treatment		0.238	**0.044**	0.097	0.093	0.165
Year × Treatment		0.648	0.854	0.915	1.000	0.775
WINES						
Year	Treatment	Alcohol (% vol.)	Titratable acidity ($g\,L^{-1}$)	pH	Malic acid ($g\,L^{-1}$)	Tartaric acid ($g\,L^{-1}$)
2012	R	13.5 ± 0.3	7.1 ± 0.5	3.09 ± 0.10	1.8 ± 0.2	3.3 ± 0.5
	SI	13.3 ± 0.2	7.7 ± 0.5	2.87 ± 0.15	1.9 ± 0.1	3.9 ± 0.6
2013	R	14.1 ± 0.3	6.6 ± 0.1	3.14 ± 0.08	2.2 ± 0.2	2.1 ± 0.5
	SI	13.7 ± 0.8	7.3 ± 0.3	3.01 ± 0.13	2.2 ± 0.1	3.0 ± 0.5
2014	R	14.7 ± 0.3	7.5 ± 0.2	3.21 ± 0.04	2.2 ± 0.1	3.7 ± 0.5
	SI	14.7 ± 0.2	7.9 ± 0.1	3.11 ± 0.01	2.1 ± 0.1	4.4 ± 0.2
Factorial analysis						
Year		**0.006**	0.388	0.068	**0.026**	0.498
Treatment		0.574	0.076	0.063	0.850	0.162
Year x Treatment		0.795	0.818	0.529	0.564	0.978

For each year, different letters indicate significant differences between treatments at $p < 0.05$. For the factorial analysis, p-values are shown. Bold letters indicate significant differences.

Agilent Technologies, Palo Alto, CA, USA). The column was thermostated at 22 °C. Extraction method, reagents and elution conditions are fully described elsewhere (Bouzas-Cid, Falqué, Orriols and Mirás-Avalos, 2018). Determinations were carried out in triplicate.

2.5.2. Determination of volatile compounds

Concentrations of wine volatiles were determined by gas chromatography (GC) as described elsewhere (Bouzas-Cid, Falqué, Orriols and Mirás-Avalos, 2018), thus methods are outlined briefly.

Major volatile compounds (methanol, higher alcohols, acetaldehyde, ethyl acetate, ethyl lactate, 1-hexanol, acetoine, acetol, 2-phenyl-ethanol, 2,3-butanediol *levo*, 2,3-butanediol *meso*) were determined by direct injection using a 7890A gas chromatograph (Agilent Technologies, Palo Alto, CA, USA). In this case, 50 µL of internal standard (5 $g\,L^{-1}$ of 4-methyl-2-pentanol in 50% ethanol) were added to 5 mL of wine. A 2 µL aliquot of this mixture was injected (split 1:30) into a capillary column, coated with CP-WAX 57CB (50 m × 0.32 mm, film thickness 0.2 µm; Chrompack, Middleburg, The Netherlands). The temperatures of the injector and the detector were 275 °C and 300 °C, respectively. The carrier gas was hydrogen at 3.3 mL min^{-1}, whereas the make-up gas was nitrogen at 30 mL min^{-1}. The flow rates of detector gas hydrogen and air were 40 mL min^{-1} and 400 mL min^{-1}, respectively. The oven temperature was held at 50 °C for 5 min, and then programmed to rise from 50 °C to 200 °C at 4 °C min^{-1} and, finally, held at 200 °C for 15 min.

Terpenes, C6 alcohols, volatile fatty acids, ethyl esters of fatty acids and acetates of higher alcohols were extracted according to López-Vázquez, Bollaín, Moser, and Orriols (2010), with some modifications as follows: to 100 mL of wine (diluted 1:1), internal standards were added: 100 µL of 4-decanol (0.144 mg L^{-1}) for free terpenes and C6 alcohols, and 1 mL of 1-heptanol (0.213 g L^{-1}) for acids, acetates and esters. This mixture was passed through an Isolute ENV+ SPE (1 g) cartridge (Biotage, UK) at 4-5 mL min^{-1}. Then, this sample was cleaned with 15 mL of distilled water and the free aromatic fraction was diluted with 30 mL of dichloromethane and recovered in a tube. Then, 60 mL of *n*-pentane were added to the eluted, as well as anhydrous sodium sulphate for removing water from the sample. The mixture was put into a 40 °C bath with a Vigreux column with refrigeration and concentrated to 1.5 mL. The extract was injected in a 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled to a 5973N mass spectrometer (Agilent Technologies, Palo Alto, CA, USA) with a single quadrupole analyser.

For terpenes and C6 alcohols, extracts (2 µL) were injected (split 1:10) into a polyethyleneglycol HP-Innowax capillary column (30 m × 0.25 µm × 0.25 mm inner diameter; Agilent Technologies, Palo Alto, CA, USA). The temperature of the injector was 250 °C. The oven temperature was held at 35 °C for 2 min, then programmed to rise to 60 °C at a rate of 30 °C min^{-1}, then at 2 °C min^{-1} till 160 °C and at a rate of 3 °C min^{-1} till 230 °C, and, finally, held at 230 °C for 10 min. The carrier gas was helium (99.999%) at 1 mL min^{-1}. Transfer line was kept at 220 °C, whereas ionization source and quadrupole temperatures were fixed at 230 °C and 150 °C, respectively. The detector was set to electronic impact mode (70 eV), with an acquisition range from *m/z* 30 to 300.

The determination of volatile fatty acids, ethyl esters and acetates of higher alcohols was carried out using the same column as that for terpenes and C6-alcohols but under different conditions. Extracts (3 µL) were injected in split mode (1:7.7), injector temperature was 230 °C, He as carrier gas at 1.3 mL min^{-1}. The oven temperature was held at 45 °C for 2 min, and then programmed to rise from 45 °C to 230 °C at 3 °C

Table 2
Irrigation effects on the amino acid concentrations (mean ± standard error, mg L^{-1}) of musts from Godello in Ribeiro. The significances of the factors year and treatment, as well as their interaction are also shown. R = rain-fed, SI = supplementary irrigation.

Compound	2012		2013		2014		Treatment	Year	Treatment × Year
	R	SI	R	SI	R	SI			
Aspartic acid	24.2 ± 4.3	23.0 ± 4.3	39.7 ± 6.0	36.6 ± 3.3	28.1 ± 1.4	29.9 ± 1.5	ns	ns	ns
Glutamic acid	46.4 ± 9.5	37.7 ± 8.3	84.5 ± 11.4	92.0 ± 15.4	85.2 ± 2.6	86.1 ± 2.4	ns	**	ns
Asparagine	4.9 ± 1.0	3.5 ± 1.6	1.9 ± 0.3	2.4 ± 0.5	31 ± 0.4	3.4 ± 0.4	ns	ns	ns
Serine	3.7 ± 3.0	31.4 ± 4.9	24.5 ± 2.4	30.9 ± 3.5	28.5 ± 1.7	29.4 ± 1.9	ns	ns	ns
Glutamine	57.4 ± 8.2	51.1 ± 10.7	34.8 ± 5.4	54.7 ± 9.6	62.7 ± 9.9	66.2 ± 8.7	ns	ns	ns
Histidine	17.6 ± 2.8	13.8 ± 4.1	8.1 ± 1.3	11.0 ± 2.0	11.1 ± 1.4	11.6 ± 1.4	ns	ns	ns
Glycine	4.4 ± 0.6	3.3 ± 0.9	2.4 ± 0.2	2.9 ± 0.4	3.3 ± 0.2	3.2 ± 0.2	ns	ns	ns
Threonine	59.0 ± 7.7	53.8 ± 11.5	34.6 ± 3.7	46.0 ± 6.9	40.9 ± 2.8	44.5 ± 3.4	ns	ns	ns
Arginine	175.7 ± 43.1	121.7 ± 42.3	62.1 ± 11.5	92.8 ± 23.4	129.5 ± 18.8	159.8 ± 23.2	ns	ns	ns
Alanine	67.5 ± 11.5	52.7 ± 9.6	34.1 ± 6.0	49.1 ± 8.5	66.8 ± 5.5	70.2 ± 6.5	ns	ns	ns
γ-Aminobutyric acid (GABA)	92.3 ± 5.8	83.4 ± 5.7	29.5 ± 3.9	44.5 ± 9.1	30.5 ± 1.0	29.6 ± 1.0	ns	***	ns
Proline	**1.7 ± 0.1 b**	**1.4 ± 0.1 a**	3.5 ± 0.9	4.5 ± 1.1	1.2 ± 0.2	1.9 ± 0.2	ns	ns	ns
Tyrosine	4.1 ± 0.8	3.5 ± 0.5	27 ± 0.4	3.2 ± 0.2	**1.7 ± 0.1 a**	**2.4 ± 0.1 b**	ns	***	ns
Ammonium ion	89.6 ± 5.6	113.8 ± 15.3	142.0 ± 8.7	175.1 ± 14.5	86.9 ± 13.2	112.2 ± 12.6	ns	ns	ns
Valine	16.9 ± 1.2	14.4 ± 1.3	13.6 ± 2.1	15.4 ± 3.0	15.2 ± 0.7	15.3 ± 0.7	ns	ns	ns
Methionine	1.9 ± 0.3	1.5 ± 0.0	1.5 ± 0.2	1.3 ± 0.1	1.2 ± 0.1	1.1 ± 0.1	ns	**	ns
Cysteine	2.3 ± 0.1	1.8 ± 0.2	2.1 ± 0.1	2.3 ± 0.1	1.6 ± 0.1	1.4 ± 0.0	ns	*	ns
Isoleucine	7.8 ± 0.5	6.9 ± 0.8	5.5 ± 0.8	6.7 ± 1.0	6.2 ± 0.4	6.3 ± 0.3	ns	ns	ns
Tryptophan	7.4 ± 1.4	5.6 ± 2.5	5.5 ± 0.6	6.0 ± 0.6	3.2 ± 0.8	3.2 ± 0.5	ns	*	ns
Leucine	10.3 ± 1.2	8.2 ± 1.2	5.9 ± 1.1	7.1 ± 1.2	7.0 ± 0.3	7.7 ± 0.4	ns	ns	ns
Phenylalanine	9.0 ± 0.9	9.6 ± 0.8	7.8 ± 1.0	9.2 ± 1.3	8.6 ± 0.6	9.0 ± 0.4	ns	ns	ns
Ornithine	0.6 ± 0.1	0.6 ± 0.1	0.4 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	ns	ns	ns
Lysine	3.7 ± 0.5	3.0 ± 0.6	2.1 ± 0.2	2.9 ± 0.4	3.2 ± 0.3	3.2 ± 0.3	ns	ns	ns
Sum of amino acids	648.9 ± 101.6	531.8 ± 106.3	406.8 ± 51.7	522.1 ± 76.4	539.6 ± 45.4	586.3 ± 52.4	ns	ns	ns

Different letters indicate significant differences between treatments at $p < 0.05$ for a given amino acid in a given year. Bold letters are used to highlight significant differences between treatments for a given amino acid in a given year. The significance of the year, treatment and their interaction is expressed as ns = non-significant; *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$.

min^{-1}, and finally held at 230 °C for 10 min. Transfer line was kept at 220 °C, whereas ionization source and quadrupole temperatures were fixed at 230 °C and 150 °C, respectively. The detector was set to electronic impact mode (70 eV), with an acquisition range from *m/z* 25 to 220.

Identification was performed using the NIST Mass Spectral library by comparing mass spectra and retention times with those of pure standard compounds. For quantification, calibration curves for each single compound were built as a function of the internal standards. These yielded regression coefficients greater than 0.99 in all cases, indicating excellent linearity. All determinations were carried out in triplicate.

The odour activity value (OAV) of each compound was calculated by dividing its concentration to its odour threshold, thus estimating its potential contribution to wine aroma (Ferreira, López, & Cacho, 2000; Guth, 1997).

2.6. Statistical analysis

Analysis of variance (ANOVA) considering year, treatment (rain-fed or supplementary irrigation) and their interaction as factors was used. Principal Component Analysis (PCA) was carried out for separating must samples according to their amino acid concentrations. Statistical analyses were carried out using R software v3.4.1 (R Core Team, 2017).

3. Results and discussion

Physiological, vegetative growth and yield data, as well as further details about the experimental design, have been reported elsewhere (Trigo-Córdoba et al., 2015). In summary, vines from the rain-fed treatment showed more negative midday stem water potentials than those from the SI treatment during the three studied years; whereas no significant differences in yield were observed. In 2014, pruning weight was higher in vines from the SI treatment (Supplementary Table 2).

3.1. General parameters of musts and wines

Year exerted a significant effect on total soluble solids (TSS), total acidity (TA) and tartaric acid concentrations of the musts, whereas treatment only affected TA (Table 1). Moreover, a trend ($p < 0.1$) to lower pH values and higher malic acid concentrations in the musts from the SI treatment was observed. No significant interactions between factors were detected. Despite more negative stem water potentials detected for grapevines under the rain-fed conditions, the absence of an effect of SI on must attributes is expected because of the mild to moderate water stress conditions observed in the study site (Trigo-Córdoba et al., 2015), and are consistent with previous studies on white cultivars in cool-humid regions (Balint & Reynolds, 2017). These results confirmed the great influence of weather conditions on must attributes and reflect the fact that vines under both treatments developed an adequate leaf surface in the first part of the growing season (Trigo-Córdoba et al., 2015). Moreover, the vines were grafted onto 196-17C rootstock, which is rather toleratant to drought and this could also have influenced the results observed.

The most sensitive trait to the effects of SI was TA. Moreover, in 2014, musts from the SI treatment had significantly lower TSS and pH values, and greater TA and tartaric acid concentrations than those from the rain-fed treatment (Table 1). These results pointed out that SI may alter must composition in the longer term and can be used as a tool for modulating must attributes (Jackson & Lombard, 1993), even under sub-humid climates.

In the case of wines, year exerted a significant influence on alcohol and malic acid contents (Table 1). In contrast, supplementary irrigation did not have a significant effect on any of the attributes considered, although a trend ($p < 0.1$) to higher TA and lower pH values in the wines from the SI treatment was observed. No significant interactions between factors were detected (Table 1). These results indicate that the severity of water stress experienced by Godello vines grafted onto 196-17C rootstock was not enough for altering the main wine attributes, as previously observed for Chardonnay under cool climate conditions

(Balint & Reynolds, 2017).

3.2. Amino acids profiles of musts and wines

The concentrations of free amino acids in Godello musts were within previously reported ranges, except for proline with concentrations between 1.2 and 4.5 mg L^{-1} (Table 2), when it has been reported to vary from 9 to 2257 mg L^{-1} (Bell & Henschke, 2005), depending on grape cultivar, maturation status, climate and management practices.

Godello can be considered an arginine accumulator cultivar, similarly to Syrah, Merlot (Garde-Cerdán et al., 2009), Garnacha and Pinot Noir (Bell & Henschke, 2005). In fact, arginine represented about 22% of the total free amino acids in Godello musts, independently of the treatment (Supplementary Figure 1). Other amino acids present at relevant concentrations in Godello musts were glutamic acid (13%), alanine (10%), glutamine (9%) and γ-aminobutyric acid (GABA, 9%). These compounds were also abundant in musts from other Spanish white varieties, such as Verdejo and Albariño (Bouzas-Cid, Díaz-Losada, Trigo-Córdoba, Falqué, Orriols, Garde-Cerdán, & Mirás-Avalos, 2018; Ortega-Heras et al., 2014).

In the current study, SI did not affect the concentrations of any of the amino acids determined in the musts, except for a decrease in proline in 2012 and an increase in tyrosine in 2014 (Table 2). However, the year exerted a significant influence on the concentrations of glutamic acid, GABA, tyrosine, methionine, cysteine and tryptophan (Table 2), likely due to the different weather conditions occurred in each year. No significant interactions between supplementary irrigation and year were detected.

Principal component analysis (PCA) was run on the covariance matrix of the concentrations of the most abundant amino acids in musts. The two first principal components (PC) explained 92.9% of the total variance in the dataset: PC1 accounted for 67.4% and PC2 for 25.5% (Fig. 1). Samples were separated according to year, whereas supplementary irrigation had less influence on the concentrations of amino acids. Musts from 2012 were located in the positive sides of PC1 and PC2, due to their high concentrations of GABA and threonine. Musts from 2013 were located in the negative side of PC1 and they were characterized by high concentrations of aspartic acid. Samples from 2014 had high concentrations of glutamic acid, and were located on the negative sides of PC1 and PC2.

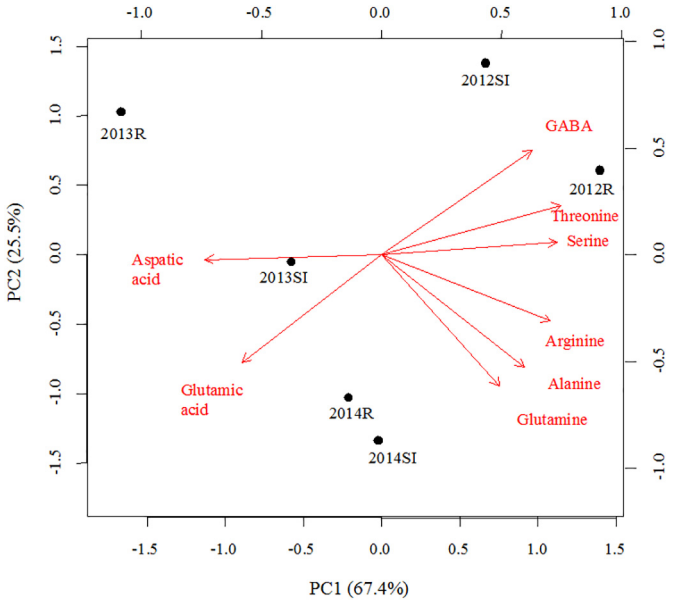

Fig. 1. Principal component analysis (PCA) of Godello musts: Biplot for the first two components (PC) for the most abundant amino acids in musts. R = Rain-fed, SI = Supplementary irrigation.

The absence of differences between treatments on the concentrations of amino acids in musts, except for single compounds in 2012 and 2014, can be explained by the mild water deficit experienced by Godello vines during the current study. Noteworthy, a white cultivar suffering from a level of water stress greater than that imposed in the current study did not show alterations on its amino acid metabolism (Deluc et al., 2009). Moreover, no significant effect of irrigation on the amino acid composition of another Spanish white cultivar (Verdejo) was detected (Ortega-Heras et al., 2014), in agreement with the results of the current study. Therefore, our data support the hypothesis that the amino acid metabolism in white cultivars of grapevine is more resistant to water stress than that of the red ones and that maturation stage and climate conditions determine the concentrations of amino acids in the musts (Deluc et al., 2009; Ortega-Heras et al., 2014).

In the case of wines, SI did not affect the concentrations of the amino acids determined, except for increasing the concentration of tryptophan in 2012, and those of glutamic acid and cysteine in 2013 (Supplementary Table 3). In contrast, year exerted a significant influence on the concentrations of glutamic acid, asparagine, serine, glutamine, histidine, threonine, tyrosine, valine, methionine, isoleucine and lysine, as well as on the sum of amino acids (Supplementary Table 3). No significant interactions between treatment and year were detected. These results are expected due to the similar amino acids composition of the musts from both treatments. Arginine and glutamine were used preferently by yeasts during fermentation, while proline and lysine were detected in greater concentrations in wines than in their corresponding musts due to yeast autolysis (Martínez-Rodríguez, Carrascosa, & Polo, 2001; Ortega-Heras et al., 2014).

3.3. Volatile composition of Godello wines

A total of 43 volatile compounds were identified in Godello wines (Table 3), including alcohols, acetates of higher alcohols, ethyl esters, fatty acids and terpenes, in concentrations similar to those reported for wines from the same variety (Losada, Andrés, Cacho, Revilla, & López, 2011; Versini, Orriols, & Dalla Serra, 1994), except for those of 2-phenylethanol and higher alcohols, which were slightly greater in the current study. This fact can be explained by the different nitrogen content of the musts and the yeast strains used in each study (Bell & Henschke, 2005).

Wines from the SI treatment showed greater concentrations of ethyl lactate and geraniol than those from the rain-fed treatment (Table 3). In contrast, the concentrations of 22 individual compounds differed significantly among the studied years. In addition, when grouped in families, year exerted a significant influence on the concentrations of acetates of higher alcohols, ethyl esters, C6-C10 volatile fatty acids and free terpenes (Table 3). No significant interactions between factors were detected except for the concentration of geraniol.

Recently, greater concentrations of alcohols, C6 compounds and phenol volatiles in wines from the Tempranillo cultivar grown under rain-fed conditions when compared to irrigated vines have been reported (Talaverano et al., 2017). These findings are in slight disagreement with the results obtained in the current study likely due to the different cultivar and climate conditions, which caused a lower level of water stress in Godello vines. Moreover, the different rootstocks used in both studies would have also altered the vegetative expression of each cultivar. In our study, soil was at field capacity during the first part of the growing season, providing adequate conditions for bud-break and the development of leaf surface (Trigo-Córdoba et al., 2015). Therefore, no restrictions on vine metabolism were expected.

Eighteen compounds were detected at concentrations above their corresponding perception thresholds (Table 4), likely contributing to wine aroma (Ferreira, López, & Cacho, 2000; Guth, 1997). However, supplementary irrigation did not affect the OAV of these compounds, except for a slight increase in that of ethyl acetate in 2014. The OAV differed significantly among years in the case of 11 compounds

Table 3
Irrigation effects on the concentrations of volatile compounds (mean ± standard error) of wines from Godello in Ribeiro. The significances of the year, treatment as well as their interaction are also shown. R = rain-fed, SI = supplementary irrigation.

	2012		2013		2014		Treatment	Year	Treatment × Year
	R	SI	R	SI	R	SI			
Methanol (mg L^{-1})	21 ± 1	21 ± 1	23 ± 1	26 ± 1	16 ± 1	16 ± 0	ns	*	ns
Ethyl acetate (mg L^{-1})	71 ± 9	81 ± 11	23 ± 1	24 ± 1	33 ± 0	38 ± 2	ns	**	ns
Acetaldehyde (mg L^{-1})	50 ± 12	55 ± 13	27 ± 2	24 ± 1	3 ± 0	3 ± 0	ns	***	ns
Higher alcohols (mg L^{-1})									
1-propanol	13 ± 1	13 ± 1	17 ± 2	21 ± 2	17 ± 2	17 ± 1	ns	ns	ns
2-methyl-1-propanol	43 ± 5	42 ± 5	31 ± 5	35 ± 1	26 ± 2	28 ± 2	ns	***	ns
2-methyl-1-butanol	51 ± 9	47 ± 7	57 ± 5	61 ± 7	49 ± 0	52 ± 2	ns	ns	ns
3-methyl-1-butanol	211 ± 29	211 ± 22	245 ± 28	281 ± 19	217 ± 5	232 ± 7	ns	ns	ns
Σ Higher alcohols	319 ± 43	312 ± 33	349 ± 39	399 ± 28	310 ± 9	327 ± 10	ns	ns	ns
Other alcohols (mg L^{-1})									
1-hexanol	1.2 ± 0.1	1.1 ± 0.1	1.3 ± 0.1	1.4 ± 0.1	1.3 ± 0.1	1.2 ± 0.1	ns	ns	ns
trans-3-hexen-1-ol	0.14 ± 0.02	0.14 ± 0.01	0.15 ± 0.01	0.15 ± 0.01	0.18 ± 0.01	0.20 ± 0.01	ns	***	ns
cis-3-hexen-1-ol	0.24 ± 0.01	0.26 ± 0.02	0.17 ± 0.01	0.20 ± 0.04	0.22 ± 0.02	0.21 ± 0.02	ns	ns	ns
Benzyl alcohol	3.15 ± 0.29	2.64 ± 0.47	2.42 ± 0.16	2.40 ± 0.18	< LOD	< LOD	ns	ns	ns
2-phenylethanol	28 ± 6	26 ± 2	40 ± 1	44 ± 6	32 ± 1	34 ± 0	ns	ns	ns
Other compounds (mg L^{-1})									
Ethyl lactate	10 ± 1	11 ± 1	**6 ± 0 a**	**7 ± 0 b**	5 ± 1	7 ± 1	*	***	ns
Acetoíne	11 ± 4	12 ± 4	5 ± 1	4 ± 0	< LOD	< LOD	ns	*	ns
Acetol	48 ± 18	41 ± 9	42 ± 9	30 ± 4	7 ± 0	5 ± 1	ns	***	ns
2.3-butanediol levo	700 ± 114	684 ± 99	670 ± 7	704 ± 46	943 ± 50	993 ± 20	ns	**	ns
2.3-butanediol meso	343 ± 29	326 ± 21	344 ± 4	352 ± 11	189 ± 9	192 ± 3	ns	***	ns
Methionol	0.37 ± 0.08	0.37 ± 0.03	0.36 ± 0.06	0.28 ± 0.08	0.35 ± 0.02	0.30 ± 0.02	ns	ns	ns
Acetates of higher alcohols (mg L^{-1})									
Isoamyl acetate	0.2 ± 0.1	0.2 ± 0.0	0.4 ± 0.0	0.5 ± 0.1	1.0 ± 0.1	1.2 ± 0.1	ns	***	ns
Hexyl acetate	0.19 ± 0.00	0.25 ± 0.08	0.48 ± 0.16	0.39 ± 0.01	0.37 ± 0.05	0.27 ± 0.01	ns	ns	ns
2-phenylethyl acetate	0.05 ± 0.02	0.07 ± 0.01	0.15 ± 0.02	0.19 ± 0.04	0.08 ± 0.01	0.10 ± 0.02	ns	ns	ns
Σ Acetates of higher alcohols	0.48 ± 0.06	0.56 ± 0.06	1.02 ± 0.10	1.10 ± 0.10	1.49 ± 0.29	1.53 ± 0.33	ns	***	ns
Esters (mg L^{-1})									
Ethyl butyrate	0.12 ± 0.00	0.13 ± 0.01	< LOD	< LOD	0.07 ± 0.01	0.09 ± 0.00	ns	**	ns
Ethyl hexanoate	0.46 ± 0.04	0.46 ± 0.02	0.42 ± 0.02	0.41 ± 0.02	0.26 ± 0.02	0.29 ± 0.02	ns	***	ns
Ethyl octanoate	0.76 ± 0.11	0.83 ± 0.03	0.41 ± 0.03	0.50 ± 0.09	0.38 ± 0.02	0.44 ± 0.04	ns	***	ns
Ethyl decanoate	0.15 ± 0.04	0.20 ± 0.03	0.20 ± 0.03	0.19 ± 0.02	0.01 ± 0.00	0.01 ± 0.00	ns	**	ns
Σ Ethyl esters C6-C10	1.73 ± 0.23	1.72 ± 0.09	1.03 ± 0.08	1.10 ± 0.12	0.72 ± 0.04	0.83 ± 0.07	ns	***	ns
Volatile fatty acids (mg L^{-1})									
Isobutyric acid	2.84 ± 0.37	3.12 ± 0.12	4.03 ± 0.20	3.87 ± 0.44	2.35 ± 0.10	2.29 ± 0.05	ns	ns	ns
Butyric acid	1.84 ± 0.36	2.06 ± 0.30	1.38 ± 0.02	1.38 ± 0.01	0.89 ± 0.01	0.80 ± 0.18	ns	***	ns
Isovaleric acid	1.29 ± 0.28	1.28 ± 0.18	2.62 ± 0.25	2.82 ± 0.36	2.00 ± 0.03	2.02 ± 0.01	ns	ns	ns
Σ Volatile fatty acids C4-C5	5.97 ± 0.73	6.46 ± 0.60	8.03 ± 0.46	8.07 ± 0.78	5.24 ± 0.13	5.11 ± 0.19	ns	ns	ns
Hexanoic acid	2.96 ± 0.37	3.45 ± 0.29	2.51 ± 0.04	2.67 ± 0.17	2.13 ± 0.03	2.37 ± 0.13	ns	***	ns
Octanoic acid	2.66 ± 0.41	3.12 ± 0.33	1.89 ± 0.07	2.45 ± 0.36	2.43 ± 0.05	2.71 ± 0.13	ns	ns	ns
Decanoic acid	0.65 ± 0.16	0.84 ± 0.08	0.75 ± 0.05	0.77 ± 0.08	0.68 ± 0.03	0.75 ± 0.03	ns	ns	ns
Σ Volatile fatty acids C6-C10	6.27 ± 0.94	7.41 ± 0.68	5.15 ± 0.15	5.89 ± 0.60	5.24 ± 0.07	5.83 ± 0.29	ns	*	ns
Free terpenes (μg L^{-1})									
trans-linalool oxide (furan)[a]	6.3 ± 1.1	6.0 ± 0.6	3.4 ± 0.4	4.5 ± 0.6	6.4 ± 0.8	6.5 ± 0.8	ns	ns	ns
cis-linalool oxide (furan)[a]	1.5 ± 0.1	1.1 ± 0.2	0.7 ± 0.1	0.7 ± 0.1	1.0 ± 0.2	1.5 ± 0.2	ns	ns	ns
trans-linalool oxide (pyran)[a]	1.1 ± 0.1	1.4 ± 0.3	0.5 ± 0.0	0.7 ± 0.1	4.1 ± 0.1	3.4 ± 0.4	ns	**	ns
cis-linalool oxide (pyran)[a]	0.5 ± 0.1	0.8 ± 0.2	0.5 ± 0.1	0.5 ± 0.1	1.0 ± 0.2	0.7 ± 0.2	ns	ns	ns
Linalool (L)	< LOD	< LOD	2.7 ± 0.2	3.0 ± 0.4	7.4 ± 0.6	7.8 ± 0.2	ns	***	ns
Hotrienol (3.7-dimethyl-1.5.7-octatriene-3-ol)[a]	0.9 ± 0.2	0.9 ± 0.2	1.3 ± 0.1	1.2 ± 0.1	2.8 ± 0.3	2.6 ± 0.1	ns	***	ns
α-terpineol (αT)	**2.3 ± 0.5 a**	**3.6 ± 0.3 b**	3.7 ± 0.4	3.7 ± 0.4	1.6 ± 0.3	2.4 ± 0.2	ns	ns	ns
Citronellol (C)	< LOD	< LOD	4.5 ± 0.5	4.0 ± 0.9	18.4 ± 1.5	17.0 ± 1.3	ns	***	ns
Nerol (N)	2.2 ± 0.4	3.0 ± 0.5	< LOD	< LOD	< LOD	< LOD	ns	ns	ns
Geraniol (G)	**3.3 ± 0.8 a**	**6.0 ± 0.3 b**	4.4 ± 0.2	4.5 ± 0.4	4.6 ± 0.3	5.1 ± 0.2	**	ns	*
Σ Free terpenes (L + αT + C + N + G)	**7.8 ± 0.4 a**	**12.6 ± 0.9 b**	15.4 ± 0.5	15.2 ± 0.4	32.0 ± 4.2	32.2 ± 3.7	ns	***	ns
Hodiol I (*trans*-3.7-dimethyl-1.5-octadiene-3.7-diol)[a]	3.9 ± 1.1	6.0 ± 0.4	1.6 ± 0.1	2.4 ± 0.3	7.6 ± 1.0	7.6 ± 0.5	ns	ns	ns
2.7-dimethyloctane-4.5-diol†	95.6 ± 26.6	98.0 ± 9.9	4.1 ± 0.4	5.4 ± 1.3	119.8 ± 6.9	127.1 ± 4.4	ns	***	ns

Different letters indicate significant differences between treatments at $p < 0.05$ for a given year. Bold letters are used to highlight significant differences between treatments for a given amino acid in a given year. Bold letters are used to highlight significant differences between treatments for a given amino acid in a given year. The significance of the year, treatment and their interaction is expressed as ns = not significant; *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$. LOD means Limit of Detection.

[a] indicates that the compound is expressed in μg L^{-1} of internal standard.

Table 4
Irrigation effects on the odour activity values (mean ± standard error) of wines from Godello in Ribeiro. Odour thresholds and descriptors for each compound are displayed. The significances of the year, treatment as well as their interaction are also shown. R = rain-fed, SI = supplementary irrigation.

	Odour threshold (μg L^{-1})	Odour descriptor	2012		2013		2014		Treatment	Year	Treatment × Year
			R	SI	R	SI	R	SI			
Ethyl acetate	7500	Pineapple	9 ± 1	11 ± 2	3 ± 0	3 ± 0	**4 ± 0 a**	**5 ± 0 b**	ns	**	ns
Acetaldehyde	500	Fruity	101 ± 25	111 ± 26	35 ± 5	47 ± 3	6 ± 0	6 ± 0	ns	***	ns
Higher alcohols											
1-propanol	750	Alcohol	17 ± 1	17 ± 2	23 ± 3	29 ± 2	23 ± 2	22 ± 2	ns	ns	ns
2-methyl-1-propanol	40000	Alcohol	1 ± 0	1 ± 0	< 1	< 1	< 1	< 1	ns	***	ns
3-methyl-1-butanol	30000	Alcohol	7 ± 1	7 ± 1	8 ± 1	9 ± 1	7 ± 0	8 ± 0	ns	ns	ns
Other alcohols											
Benzyl alcohol	620	Blackberry	5 ± 1	4 ± 1	4 ± 0	4 ± 0	< 1	< 1	ns	***	ns
2-phenylethanol	14000	Rose	2 ± 0	2 ± 0	3 ± 0	3 ± 0	2 ± 0	2 ± 0	ns	ns	ns
Other compounds											
Acetoine	10000	Butter, almond	1 ± 0	1 ± 0	< 1	< 1	< 1	< 1	ns	***	ns
Acetates of higher alcohols											
Isoamyl acetate	30	Banana	8 ± 1	8 ± 2	17 ± 3	13 ± 1	39 ± 4	35 ± 3	ns	***	ns
Esters											
Ethyl butyrate	20	Fruity	7 ± 1	6 ± 0	< 1	< 1	5 ± 0	4 ± 0	ns	ns	ns
Ethyl hexanoate	14	Fruity	33 ± 1	33 ± 3	29 ± 1	30 ± 1	21 ± 2	19 ± 1	ns	***	ns
Ethyl octanoate	5	Fruity	166 ± 6	153 ± 21	99 ± 18	82 ± 7	89 ± 9	75 ± 5	ns	***	ns
Ethyl decanoate	200	Grape	1 ± 0	< 1	1 ± 0	1 ± 0	< 1	< 1	ns	**	ns
Volatile fatty acids											
Isobutyric acid	2300	Cheese	1 ± 0	1 ± 0	2 ± 0	2 ± 0	1 ± 0	1 ± 0	ns	ns	ns
Butyric acid	173	Cheese	12 ± 2	11 ± 2	8 ± 0	8 ± 0	5 ± 1	5 ± 0	ns	***	ns
Isovaleric acid	33	Cheese	39 ± 5	39 ± 9	86 ± 11	80 ± 7	61 ± 0	61 ± 1	ns	ns	ns
Hexanoic acid	3000	Cheese	8 ± 1	7 ± 1	6 ± 0	6 ± 0	6 ± 0	5 ± 0	ns	***	ns
Octanoic acid	500	Rancid	6 ± 1	5 ± 1	5 ± 1	4 ± 0	5 ± 0	5 ± 0	ns	ns	ns

Different letters indicate significant differences between treatments at $p < 0.05$ for a given year. The significance of the year, treatment and their interaction is expressed as ns = not significant; *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$. Only the compounds with odour activity values greater than 1 are shown. Odour thresholds have been taken from Guth (1997) and Ferreira et al. (2000).

(Table 4). No significant interactions between factors were observed.

In the studied wines, higher alcohols were detected at concentrations greater than 300 mg L^{-1} (Table 3), which could lead to negative effects on wine aroma since the concentrations of 1-propanol and 3-methyl-1-butanol surpassed their corresponding OAV (Table 4). Higher alcohol concentrations in the wines showed no differences between treatments in the current study, likely due to the low to mild water stress experienced by Godello vines (Trigo-Córdoba et al., 2015). These findings are in agreement with studies for other cultivars (Qian, Fang, & Shellie, 2009), but contrast with reported reductions in 2+3-methyl-1-butanol caused by irrigation (Talaverano et al., 2017). Several aspects that differ among studies, such as cultivar, rootstock, climate conditions and soil type, might have caused these contrasting results.

Godello wines are characterized by a prevalence of *cis*-3-hexen-1-ol on its *trans* isomer (Versini, Orriols, & Dalla Serra, 1994), as observed in the current study. In addition, benzyl alcohol and 2-phenylethanol showed OAV > 1 in the studied wines (Table 4). These compounds impart blackberry and flower notes to wines, respectively (Francis & Newton, 2005; Rapp & Mandery, 1986). However, we did not detect differences between treatments in the current study.

Three acetates of higher alcohols were determined in Godello wines (Table 3) at lower concentrations than in other studies (Blanco, Mirás-Avalos, Pereira, & Orriols, 2013; Losada, Andrés, Cacho, Revilla, & López, 2011), likely due to the different yeast strains used (Bell & Henschke, 2005). Supplementary irrigation did not affect the concentrations of these compounds in the current study. For every treatment and year, isoamyl acetate was present at OAV greater than 8, providing banana notes to the studied wines; whereas the other acetates of higher alcohols were found in concentrations lower than their detection thresholds.

Volatile fatty acids appeared at concentrations greater than their perception thresholds, being responsible for “rancid” and “cheese” aromas (Robinson et al., 2014). Supplementary irrigation did not exert a significant influence on the concentrations of fatty acids, as already observed in Tempranillo wines (Talaverano et al., 2017).

Most of the esters identified in the current study were ethyl esters of fatty acids (Table 3), but supplementary irrigation did not affect their concentrations. These compounds usually play a positive role in wine quality, providing fruity aromas (Rapp & Mandery, 1986). For instance, ethyl octanoate provides odours of pineapple, pear and sweet fruit, while ethyl hexanoate gives aroma of green apple. These two compounds are characteristic of the aroma profile of young white wines such as those from Godello (Losada, Andrés, Cacho, Revilla, & López, 2011). In the current study, these esters surpassed their detection thresholds at least during one of the studied years (Table 4), being a relevant part of wine aroma.

Terpenes have a relevant role in the aroma of white wines (Versini, Orriols, & Dalla Serra, 1994), since they provide floral attributes to wines. In the current study, SI significantly increased the concentration of geraniol in Godello wines (Table 3). However, terpenes appeared at concentrations lower than their perception thresholds (Table 4) and, likely, the significant differences observed between treatments and years were not enough to have an incidence at the sensory level.

When grouped in families, volatile compound concentrations differed from one year to another (Table 3). The concentrations of free terpenes and acetates increased from 2012 to 2014, whereas those of ethyl esters and volatile fatty acids were greater in 2012. These inter-annual variability could be explained by the different weather conditions occurred in each year, which might have caused different maturation of the grapes.

3.4. Relationships among amino acids and volatiles

Significant linear correlations among must amino acids and wine

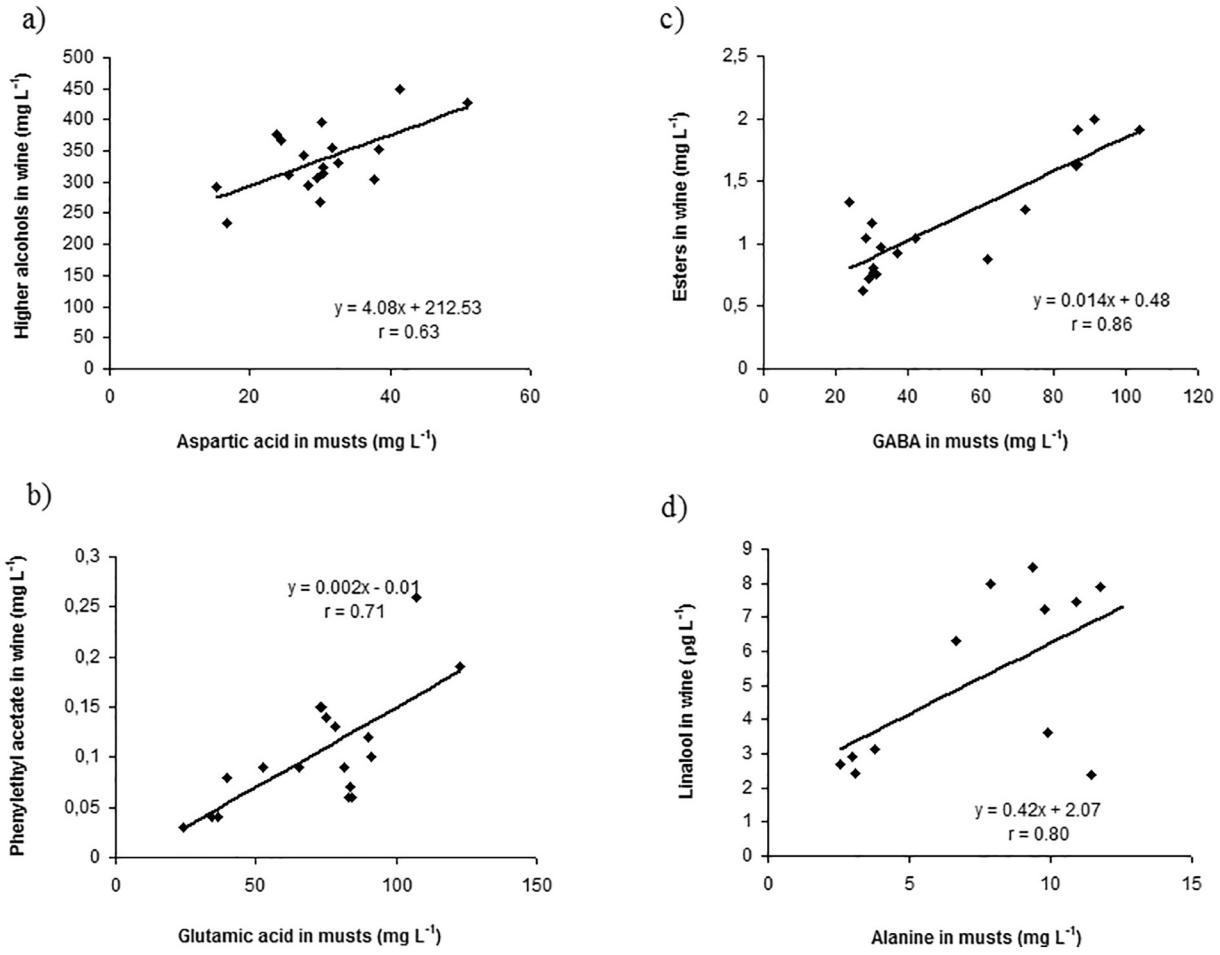

Fig. 2. Relationships between some amino acids in the musts and volatile compounds in wines: a) Aspartic acid and higher alcohols; b) Glutamic acid and phenylethyl acetate; c) GABA and esters; d) Alanine and linalool.

volatiles were detected. For instance, glutamic acid concentration in musts correlated to that of 23 individual volatile compounds in wines, whereas leucine concentration in must was only related to three volatiles. As an example, Fig. 2 displays the relationships between aspartic acid and higher alcohols; glutamic acid and phenylethyl acetate; GABA and esters; and alanine and linalool. As observed in Fig. 2, these correlations were positive, although data dispersion was important.

Esters in wines correlated positively with the concentration of some amino acids in the fruit (Guitart, Hernández-Orte, Ferreira, Peña, & Cacho, 1999), as the case of GABA in the current study (Fig. 2). These compounds provide fruity aromas and flavours to wines (Ebeler, 2001); hence, the amino acid concentrations in the must might have affected wine sensory properties. In the current study, wines from the two treatments did not differ on ethyl ester concentrations; therefore, a similar fruity aroma is expected. This might have been caused by the low level of water stress experienced by Godello vines (Trigo-Córdoba et al., 2015) and suggests that rainfall amount was enough to cover the Godello grapevine water needs during the current study.

4. Conclusions

Under the climate conditions of Northwest Iberian Peninsula, titratable acidity of Godello musts increased with supplementary irrigation; whereas amino acid concentrations were not altered by water application. However, some volatile compounds, such as ethyl lactate and geraniol, were determined in greater concentrations in wines issued from the supplementary irrigation treatment. In conclusion, despite the fact that supplementary irrigation affected must and wine composition in specific cases, climate conditions have been determinant in the results obtained in this study.

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Conflict of interest

The authors declare that they have no conflict of interest.

Appendix A. Suppelementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodres.2018.05.074.

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